



# Potential Impacts on Air Quality of the Use of Ethanol as an Alternative Fuel

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## Objective

To obtain a better understanding of the potential effects of alcohol fuels on air quality in urban and regional areas by obtaining field and laboratory data to specifically examine the possible impacts of ethanol (ETOH)/gasoline fuel blends by taking measurements in Albuquerque, New Mexico, when these fuels are used. Another objective of this project is to evaluate and develop new methods for measurement of oxygenates and for using natural carbon-isotopic signatures as a means of determining the relative source strengths of aldehydes from ethanol and fossil-based fuels.



Map of Albuquerque

## Approach

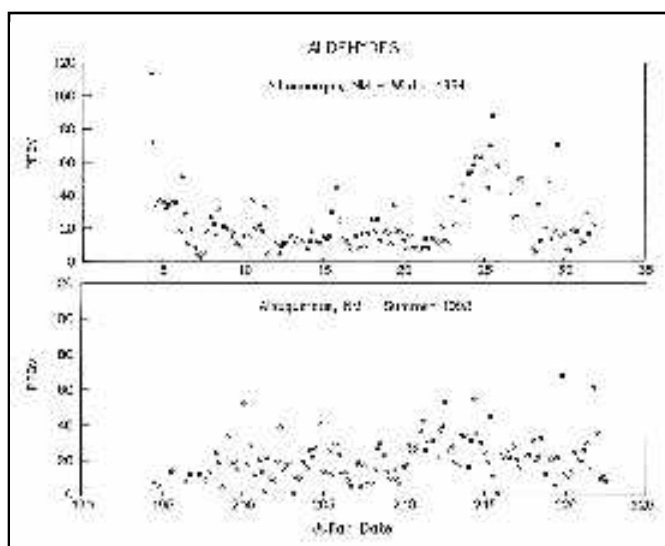
Field studies were conducted in Albuquerque, New Mexico, during the summer of 1993, the winter of 1994, and the winter of 1995 to compare air quality when ethanol/gasoline blends were absent and in use. Specific attention was given to aldehydes (acetaldehyde and formaldehyde) and peroxyacetyl nitrate (PAN) as these pollutants are likely to increase because of increased primary emission of acetaldehyde when ethanol/gasoline blends are used for motor vehicles. The field work was performed collaboratively with New Mexico Tech and the City of Albuquerque's Environmental Health Department Air Pollution Control Division at a centrally located sampling site in Albuquerque (see site map).

Measurements of ozone ( $O_3$ ), nitrogen oxides ( $NO_x$ ), carbon monoxide (CO), PAN, aldehydes, organic acids, daytime temperature, and ultraviolet-B (UV-B) radiation were taken using a wide variety of analytical instrumentation. Analyses of the data, particularly the formaldehyde/acetaldehyde ratios, were performed to aid in assessing the potential importance of primary emissions of acetaldehyde from ETOH in the fuel mixtures.



The potential for using CO and CO<sub>2</sub> isotopic analysis to determine the relative amounts of various hydrocarbon (HC) sources (natural versus anthropogenic) using infrared (IR) techniques was examined. Photolysis of aldehydes to form CO and CO<sub>2</sub> and long-path high resolution infrared spectroscopy were used to determine the <sup>13</sup>C/<sup>12</sup>C isotopic ratios. Isotopic standards were measured using this approach for direct comparison of the method.

The use of ozone chemiluminescent reactions with oxygenates and other hydrocarbon species at high temperature (170°C) was examined and the technique compared to a flame ionization detector (FID) to evaluate this method for aldehyde and oxygenate measurements (e.g., ethers, ketones, etc.).



## Accomplishments

The field studies completed in Albuquerque have shown that the use of ETOH/gasoline blends are affecting the levels of aldehydes and PAN during the winter periods when the fuel blends were used. As well, natural hydrocarbon emissions from vegetation (principally isoprene) are causing increased levels of aldehydes during summer months and may play an important role in urban as well as regional atmospheric chemistry.

Infrared spectroscopic methods can allow stable carbon isotopic determinations of organic aldehydes to be performed based on laboratory studies. Improvements can be obtained by using a higher precision total pressure measurement. The ozone chemiluminescent detection of

oxygenates using a gas chromatographic system looks very promising for higher oxygenates (acetaldehyde and larger aldehydes, ketones, ethers, including methyl tertiary butyle ether, etc.). Detection sensitivities of 10-100 times that for an FID were observed when the detector was operated at 170°C.

## Future Direction

Carbon isotopic signatures as a means of separating the various sources of organic oxygenate emissions looks very attractive, especially for ethanol produced from corn, which will be enriched in <sup>13</sup>C. Future efforts examining the use of carbon isotope signatures for source apportionment and the further development of ozone chemiluminescent measurement of aldehydes and other oxygenates are needed to further improve our understanding of the potential impacts of ethanol and other oxygenated fuels on air quality.

## Publications

C.J. Popp, L. Zhang, and J.S. Gaffney, "Organic Carbonyl Compounds in Albuquerque, New Mexico Air: A Preliminary Study of the Effects of Oxygenated Fuel Use." *Alternative Fuels and the Environment*. Francis Sterret, ed., CRC Press, Inc., Boca Raton, FL. Chapter 4, pp. 61-74 (1995).

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N.A. Marley, J.S. Gaffney, and Y.-H. Chen, "Chemiluminescent Detection of Organic Air Pollutants." In *Proceedings of the Second Annual ANL Technical Women's Symposium*, Argonne, IL, in press (1996).

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